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ABSTRACT

Over the last two decades, a substantial effort has been devoted to the design of molecules with enhanced NLO responses. It has become increasingly clear over recent years that multipolar structures offer challenging possibilities in this respect. In particular, the octupolar framework provides an interesting route towards enhanced NLO responses and improved nonlinearity-transparency trade-off. In this perspective, we have implemented an innovative route based on octupolar structures derived from the boroxine ring. By grafting three electron-donating appendices on the electron-deficient boroxine core, octupolar quasi-planar molecules displaying markedly improved nonlinearity-transparency trade-off, as compared to the prototypical octupole (TATB) or the extensively studied triazine derivatives, were designed. This route indeed led to octupolar molecules showing $\beta(0)$ values (from calculations and solution measurements) larger than that of TIATB while remaining blue-shifted by nearly 100 nm and totally transparent in the visible region. Combined experimental and theoretical investigations reveal that this behavior is related to a periphery-to-core intramolecular charge transfer phenomenon in relation with the low-aromaticity and electron-withdrawing character of the boroxine ring. This study opens a new route for molecular engineering of transparent octupolar derivatives for NLO, including the design of effective materials for SHG in the visible-blue region.

Keywords: octupoles, first hyperpolarizability, HLS, boroxines, quantum chemistry.

1. INTRODUCTION

The field of molecular nonlinear optics (NLO) has attracted increasing attention over the past twenty years,[1-3] owing to its connection with essential issues such as charge transfer, (hyper)polarizabilities, conjugation, as well as to various applications in different fields including material science (telecommunications,[4] optical data storage and information processing,[5] microfabrication[6-8]) as well biological imaging…[9,10] Second-order NLO effects such as second harmonic generation (SHG) or electro-optic modulation (EOM) require the design of chromophores that exhibit enhanced quadratic responses. Molecular engineering of one-dimensional (1-D) chromophores has been particularly active, leading to push-pull derivatives displaying giant off-resonance first-order (β)[11,12] hyperpolarizabilities. Such chromophores however display an intense absorption band in the visible region due to a strong intramolecular charge transfer (ICT) transition. Novel strategies were thus needed for optimizing the efficiency-transparency trade-off, especially in the context of the search for effective materials for SHG in the visible. In this perspective, the octupolar route pioneered by Lehn, Zyss and coworkers[13,14] offers a wide range of possibilities towards enhanced NLO responses. The octupolar structures also offer interesting potentialities for the design of EOM materials that would be insensitive to polarization.

These attractive features have prompted numerous studies devoted to novel multidimensional and multipolar structures taking advantage of the tensorial nature of hyperpolarizabilities,[3,15,16] 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) being the prototypical structure.[13,17-19] A range of octupolar molecules with a two-dimensional (2D) character and a threefold rotational symmetry axis have been investigated such as those derived from trisubstituted benzenes[20,21] (in particular triphenylbenzenes[22-25]) and hexasubstituted benzenes[19,26,27] (in particular tricyanobenzenes,[28-30]

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trinitrobenzenes,[31] and trimethoxybenzenes[32]), 1,3,5-triazines,[20,26,27,33-36] triarylamines,[37-40] hexaazatriphenylenes,[41] calixarenes,[42] tricyanomethanide anion,[43] crystal violet[19,21,44,45] and other triarylmethyl cations,[36,46] cyclopropenylium[19], and cyanines.[26,47] 3D octupolar molecules of approximated tetrahedral symmetry have also been designed.[40,48-53]

In this general framework, our goal has been the design of novel octupolar systems exhibiting both improved transparency **and** higher nonlinearity than TATB or the widely studied octupolar triazine derivatives. Our approach isbased on the functionalization of an heterocyclic moiety, the boroxine core (Fig. 1), which is both stable, planar, electron-deficient and has low-aromaticity. Surprisingly, the potentialities of molecular boroxine derivatives for NLO have not overlooked until recently,[54] though boron inorganic crystals - such as BBO which is widely used in wavelength conversion devices[55] - have long been know to display interesting NLO properties. We have thus investigated a series of three octupolar molecules built from the boroxine ring via the symmetrical grafting of three electron-releasing groups on the electron-deficient core (Fig 1). By increasing the electron-donating strength of the substituents, we were aiming at increasing their quadratic hyperpolarizabilities.[56] Phenyl units were selected as rigid linkers between the substituents and the core so as to allow periphery-to-core intramolecular charge-transfer to take place while maintaining suitable transparency. Due to the absence of steric hindrances and in contrast with trisubstituted benzenes[20,21] triarylboroxines usually lead to quasi planar structures[57] This is a common feature with octupolar triazines derivatives that have been investigated for optimization of the nonlinearity-transparency trade-off.[20,26,27,35] However, the boroxine shows much lower aromatic character,[58] which is expected to lead to higher nonlinear optical responses.

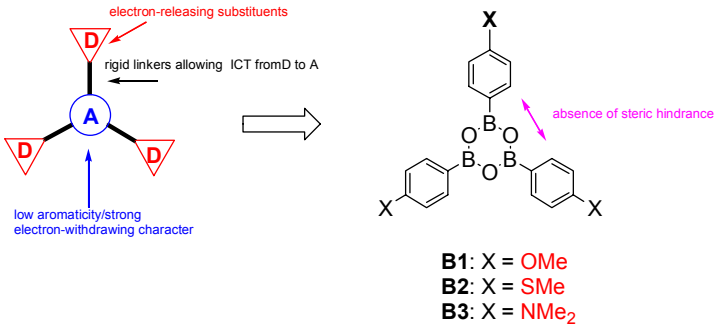

Fig. 1. Molecular engineering of octupolar derivatives derived from the boroxine ring.

2. METHODOLOGY

2.1. Materials

Triarylboroxines are easily obtained from the corresponding boronic acids via a dehydration reaction leading to the corresponding cyclic trimeric anhydride (Figure 2). Interestingly, the presence of electron-donating substituents has been reported to increase the stability of triorganoboroxine derivatives towards hydrolysis.[59]

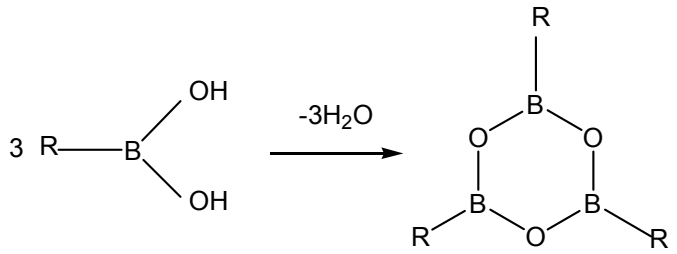

Fig. 2. Synthetic route towards generic compounds **Bx**.

2.1. Linear and non linear optical measurements

Absorption and harmonic light scattering (HLS) measurements have been performed for molecules **B1-B3** in chloroform. UV/VIS spectra were recorded on a Jasco V-570 spectrophotometer. The first hyperpolarizabilities β of octupolar molecules were determined by HLS experiments in solution performed at 1.064 mm locating the second harmonic signal in the transparency region. This procedure avoids possible contamination of the HLS signal by two-photon excited fluorescence. In addition, the boroxines **B1-B3** did not show any detectable fluorescence when excited in their absorption band.

Firstly introduced by Terhune and Maker,[60,61] the technique of HLS experiments is based on the analysis of the incoherent scattered second harmonic signal from an isotropic medium. It is particularly useful to investigate multipolar molecules and ionic species not tractable with EFISH.[62,63] As resulting from an incoherent process, the scattered nonlinear intensity $I^{2\omega}$ can be expressed as $I^{2\omega} = G\left(N_1 \langle \beta_1^2 \rangle + N \langle \beta^2 \rangle\right)\left(I^{\omega}\right)^2$ for a solution with N (N_1) chromophores (solvent) per ml of solution. Here G embodies geometrical factors and experimental correction terms and the brackets refer to statistical isotropic orientational averaging. G evaluation proceeds from the calibration of the experiment, by means of a reference CCl_4 solution with $\sqrt{\langle \beta_1^2 \rangle} = 0.26\ 10^{-30}$ esu.[24,25] $\sqrt{\langle \beta^2 \rangle}$ of the solute molecules is derived from the determination of the linear dependence of the harmonic intensity as a function of the square of the fundamental intensity I^{ω} for different molecular concentrations. Measurements were carried out in chloroform with pure solvent, leading to $\sqrt{\langle \beta_1^2 \rangle} = (0.19 \pm 0.03)\ 10^{-30}$esu.[17] The corresponding static values $\beta_{HLS}(0)$ were calculated using a degenerated three-level dispersion factor.[2] The modulus $||\beta|| = \sqrt{\sum_{ijk} \beta_{ijk}^2}$ is derived from β_{HLS} according to $||\beta|| = \sqrt{21/2}\ \beta_{HLS}$ for molecules with D_{3h} symmetry. The experimental values are compared to those reported for TIATB, a soluble analogue of TATB,[19] using the β^X convention.[64]

2.2. X-Ray study

The single crystal of boroxine derivative **B1** (formula: $C_{21}H_{21}B_3O_6$) used for the X-Ray study was a colorless prism, 0.6×0.45×0.2 mm with D_c = 1.271 g cm^{-3}, grown from crystallization in chloroform. X-ray diffraction data were collected using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo K radiation (=0.71073 Å) at 293 (2) K. Refinement on all 4196 reflections leads to R-factors of R_1 = 0.0502, wR_2 = 0.1184 for I > 2σ(I). Extensive crystallographic data and details can be found in CCDC 216501.

2.3. Computational details

Both solvation effects and vibrational contributions were neglected. Optimized molecular ground state geometries and electronic properties were obtained using the Gaussian 98 package[65] at the density functional theory (DFT) B3LYP[66] level using the 6-31G* basis set. Once we had verified that all compounds of the series lead to planar conformations, C_{3h} symmetry was imposed for molecules **B1** and **B2** whereas D_{3h} symmetry was assumed for derivative **B3**. Agreement with experiment was found satisfactory so that we did not found necessary to improve geometry optimization by either changing the level of theory or using a more extended basis set. First order static hyperpolarisabilities β_{ijk} were performed at both Hartree-Fock (HF) and B3LYP levels starting from the B3LYP/6-31G* optimized geometry. Whereas the B3LYP calculations of β_{ijk} require a numerical finite field procedure, HF level of theory permits analytical derivatives which, reduces both computational effort and numerical errors. Comparing results out of numerical and analytical procedure at the HF level allows us to check for possible numerical instabilities. In Gaussian 98 package,[65] β_{ijk} are given in atomic units and defined within a Taylor series expression of the dipole moment (β^T convention of ref.[64]). Experimental data being given using the β^X convention,[64] a multiplicative conversion factor of 2.1598 10^{-33} should be applied to theoretical data. For symmetry reasons, components of the first order hyperpolarisability tensor are not all independent. For a molecule with D_{3h} symmetry the only non-zero components are

$\beta_{xxx} = -\beta_{xyy} = -\beta_{yxy} = -\beta_{yyx}$ and the β modulus is given by $2\beta_{xxx}$. In the case of C_{3h} symmetry, the additional non-zero components are $\beta_{yyy} = -\beta_{yxx} = -\beta_{xyx} = -\beta_{xxy}$ and the modulus is thus given by $2\sqrt{\beta_{xxx}^2 + \beta_{yyy}^2}$.

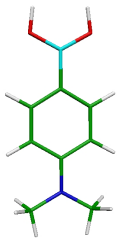

Fig. 3. Molecular geometry of dipolar model of derivative **B3**.

A dipolar model, shown in Figure 3, has been constructed to perform a limited set of test of both level of theory and basis set size. Table 1 shows that for a given basis set (6-31G*) MP2 and B3LYP level of theory lead to comparable results whereas HF estimates are 30% smaller. This is an indication that contribution due to electronic correlations might be significant in related compounds. On the other hand, when increasing the basis set size we do not observe any drastic change. We are aware that octupolar derivatives might behave differently from our dipolar model and that one should seek for more extended basis sets as it is well known that computation of accurate non-linear optical properties are much more demanding then other properties such as molecular geometries or ground state electronic properties. Nevertheless, we believe that B3LYP/6-31G* calculations are enough sufficient to discuss the trends. All calculations presented in section 3.3. are thus obtained within this approximation. As for our dipolar model, HF results for compound **B1-B3** are systematically smaller then those obtained within B3LYP.

Table 1. First order hyperpolarisability of dipolar model shown on Figure 3

	HF/6-31G*	**HF/6-311+G****	**B3LYP/6-31G***	**B3LYP/6-311G****	**MP2/6-31G***
$\|\|\beta_{calc}(0)\|\|$ (10^{-30} esu)	2.0	2.1	3.2	3.2	3.0

Illustrations were obtained with MOLEKEL.[67]

3. RESULTS AND DISCUSSION

3.1. Structure

Compound **B1** crystallizes in monoclinic space group $P2_1/n$ with a = 9.0568(2), b = 14.1334(4), c = 16.9564(7) Å, β = 104.5710(10)°, V = 2100.67(11) Å^3, Z = 4. Two different views showing crystal packing are displayed on Figure 4. View along the **a** axis (Figure 4. (left)) shows "up/down" arrangement of coplanar molecules leading to two crossing molecular sheets best seen on Figure 4 (right). The molecular structure derived from single crystal X-Ray diffraction is shown in the left part of Figure 5 as well as atomic numbering. Selected bond lengths and bond angles are listed in Table 1. The molecular structure obtained for compound **B1** is quite similar to the one reported for $Ph_3B_3O_3$ [57a] and (4-$MeC_6H_4)_3B_3O_3$,[57b] except that here intermolecular interactions supress all molecular symmetry elements. The molecule is quasi-planar, dihedral angles defined by four atoms of the boroxine ring are of about 1° and those defined between the phenyl rings and the central ring range between 2 and 10°. The boroxine ring angles are close to 120° as expected for sp^2 hybridization, with B-O-B angles slightly larger (121.1°) than the O-B-O angles (118.9°). The mean B-O bond length (1.378 Å) is significantly smaller than B-O distances reported for other boroxine octupolar derivatives (1.384-1.386 Å).[57a,b] The three phenyl rings are substantially different from each other, the average of all six C-C bond length ranging from 1.380 to 1.386 Å as a consequence of intermolecular interactions. Nevertheless, bond lengths and angles remain within normal range for phenyl rings including the smaller C-C-C angles of the boron substituted carbon (116.3°) commonly observed for other phenyl substituents.

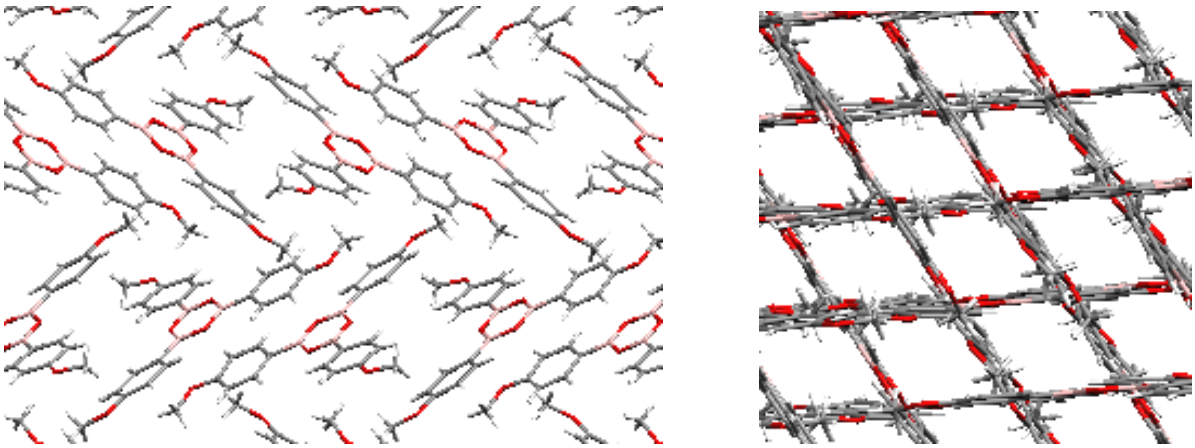

Fig. 4. Packing diagram as obtained from X-Ray measurements on compound **B1**: **(left)** view along the **a** axis, the **b** axis is horizontal and the **c** axis vertical and **(right)** view of molecular sheets.

As can be seen on Figure 5 and Table 2, the calculated molecular geometry of compound **B1** is in quite good agreement with the one deduced from X-Ray diffraction on single crystals. Most of the bond lengths are slightly overestimated with the exception of the C-O bonds connected to the phenyl ring. Bond angles are almost within experimental error for the boroxine ring. Maximum deviation is observed for the phenyl rings. Bearing in mind that molecules become deformed in the crystal due to intermolecular interactions, the global agreement between calculated and experimental values is satisfactory.

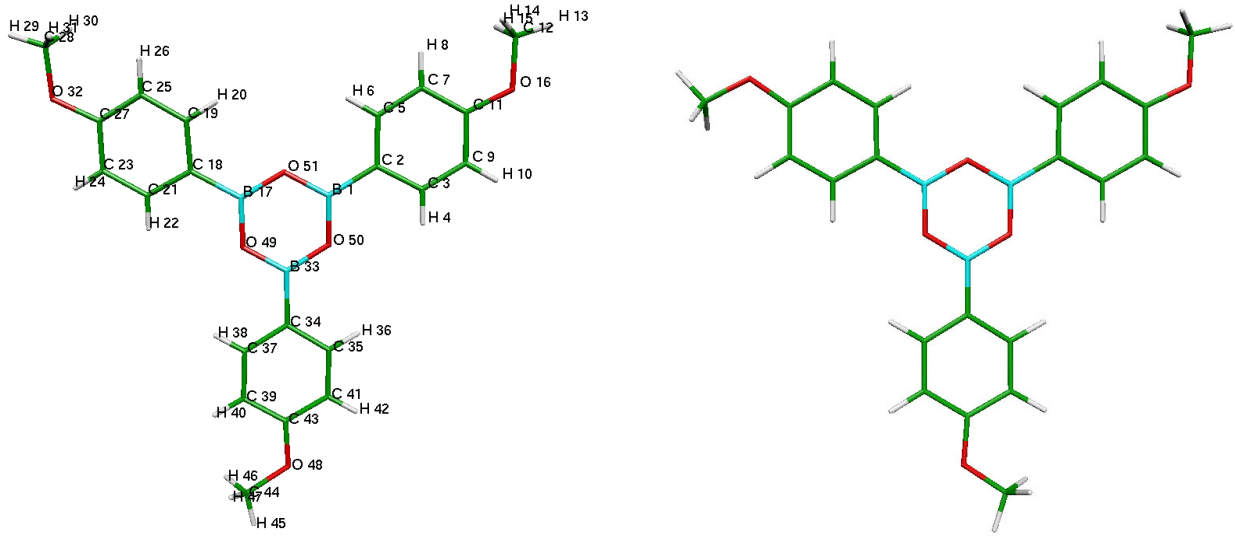

Fig. 5. **(left)** Molecular geometry of compound **B1** as obtained from X-Ray measurements showing atomic numbering. **(right)** Calculated optimized geometry of boroxine derivative **B1.**

Table 2. Experimental and calculated selected interatomic distances and bond angles of derivative **B1**.

Bond	RX	Calc.	Bond	RX	Calc.	Bond	RX	Calc.
B_1-O_{50}	1.374 (4)	1.385	C_3-C_{11}	1.380 (3)	1.405	C_{35}-C_{41}	1.375 (3)	1.386
B_1-O_{51}	1.380 (3)	1.384	C_{11}-C_7	1.380 (3)	1.402	C_{41}-C_{43}	1.393 (4)	1.405
B_{17}-O_{51}	1.379 (3)	1.385	C_7-C_5	1.388 (4)	1.394	C_{43}-C_{39}	1.380 (3)	1.402
B_{17}-O_{49}	1.378 (3)	1.384	C_5-C_2	1.384 (4)	1.404	C_{39}-C_{37}	1.376 (4)	1.394
B_{33}-O_{49}	1.379 (3)	1.385	C_{18}-C_{19}	1.384 (3)	1.411	C_{37}-C_{34}	1.391 (3)	1.404
B_{33}-O_{50}	1.379 (3)	1.384	C_{19}-C_{25}	1.379 (3)	1.386	C_{11}-O_{16}	1.366 (3)	1.362
B_1-C_2	1.547 (4)	1.547	C_{25}-C_{27}	1.374 (4)	1.405	C_{27}-O_{32}	1.377 (3)	1.362
B_{17}-C_{18}	1.542 (4)	1.547	C_{27}-C_{23}	1.375 (3)	1.402	C_{43}-O_{48}	1.364 (3)	1.362
B_{33}-C_{34}	1.543 (4)	1.547	C_{23}-C_{21}	1.377 (3)	1.394	O_{16}-C_{12}	1.417 (3)	1.420
C_2-C_3	1.389 (3)	1.411	C_{21}-C_{18}	1.394 (3)	1.404	O_{32}-C_{28}	1.425 (3)	1.420
C_3-C_9	1.372 (3)	1.386	C_{34}-C_{35}	1.401 (3)	1.411	O_{48}-C_{44}	1.423 (3)	1.420

Angle	B_{17}-O_{51}-B_1	B_1-O_{50}-B_{33}	B_{33}-O_{49}-B_{17}	O_{51}-B_1-O_{50}	O_{50}-B_{33}-O_{49}	O_{49}-B_{17}- O_{51}	
RX	121.2 (2)	120.9 (2)	121.2 (2)	119.1 (2)	119.0 (2)	118.6 (2)	
Calc.	121.3	121.3	121.3	118.7	118.7	118.7	
Angle	C_2-C_5-C_7	C_5-C_7-C_{11}	C_7-C_{11}-C_9	C_{11}-C_9-C_3	C_9-C_3-C_2	C_3-C_2-C_5	C_{11}-O_{16}-C_{12}
RX	123.0 (2)	118.9 (3)	119.4 (2)	120.7 (2)	121.8 (2)	116.3 (2)	118.4 (2)
Calc.	122.1	119.3	119.8	119.9	121.7	117.3	118.5

3.2 Optical properties

Experimental and theoretical optical properties are collected in Table 3.

Table 3. Absorption and nonlinear properties of molecules **1-3** in chloroform. Calculated maximum absorption wavelength and β modulus at B3LYP/6-31G* level. First order hyperpolarisabilities are given using β^X convention.[64]

	σ_P [a]	λ_{exp}^{max} (nm)	λ_{calc}^{max} (nm)	ε ($M^{-1}.cm^{-1}$)	FWHM [b] (cm^{-1})	$\lambda_{cut-off}$ [c] (nm)	β_{HLS} (10^{-30} esu)	$\beta_{HLS}(0)$ (10^{-30} esu)	$\|\beta_{exp}\|$ (10^{-30} esu)	$\|\beta_{exp}(0)\|$ (10^{-30} esu)	$\|\beta_{calc}(0)\|$ (10^{-30} esu)
B1 X=OMe	-0.27	241	242	$4.0\ 10^4$	1750	286	47	35	152	115	7
B2 X=SMe	0.00	270	268	$4.6.10^4$	3360	301	45	31	146	101	12
B3 X=Nme_2	-0.83	281	269	$5.8.10^4$	4350	326	83	56	249	181	13
Dipolar model			242								3
TATB[d]		351	280								4
TIATB[e]		375	310				10	4.4	32	14	6

[a] Hammett Substituent Constants for X taken from ref.[68]. [b] Halfbandwith. [c] Wavelength at which the transmittance is 95%. [d] Experimental value taken from ref.[13] [e] Experimental values are taken from. ref.[26]

3.2.1 Absorption

As can be seen on Figure 6, the molecules **B1-B3** show an intense absorption band in the UV region but maintain full transparency in the near UV-visible region ($\lambda_{cut-off} \leq 325$ nm). Compared to TIATB octupolar derivatives, the absorption is blue-shifted by about 100 nm. A crude estimate of the maximum absorption wavelength can also be deduced from the HOMO-LUMO energy gap and is reported in table 3 (λ_{calc}^{max}). The agreement between experimental and calculated values is especially good for the boroxine derivatives whereas agreement deteriorates for TATB and its soluble derivative TIATB. Nevertheless, it is well known that at the B3LYP/6-31G* level of theory, the trend of these wavelengths in homologous series is usually well described by these energy gaps whereas absolute values are much depending on the series.

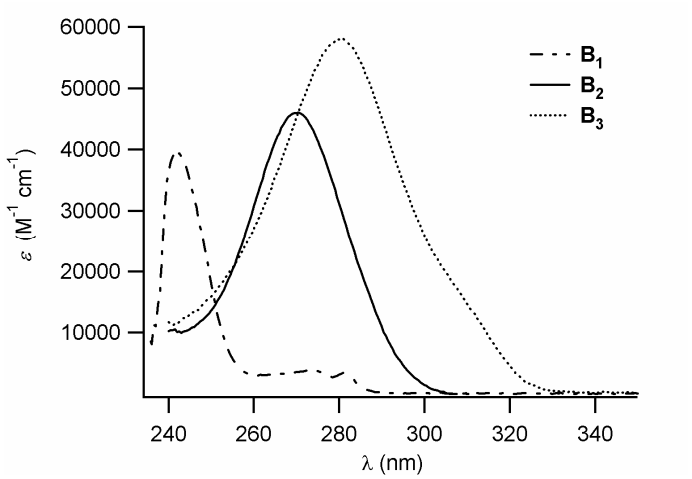

Fig. 6. Normalized absorption spectra of molecules **B1**-**B3** in chloroform.

We observe a marked bathochromic and hyperchromic shift as well as a pronounced broadening of the absorption bands in the **B1**-**B3** series (Figure 6 and Table 3). This trend is most probably correlated with an increase of the periphery to core intramolecular charge transfer in agreement with a decrease of the HOMO-LUMO gap derived from calculations. In addition, all compounds show a slight positive solvatochromic behavior, indicating a larger stabilization of the excited state as compared to the ground state by a polar solvent. This behavior suggests that significant charge redistribution is taking place upon excitation. This should be related to the periphery-to-core intramolecular charge transfer from the donating appendices to the boron atoms upon excitation which can be inferred from the frontier orbitals plotted on Figure 7.

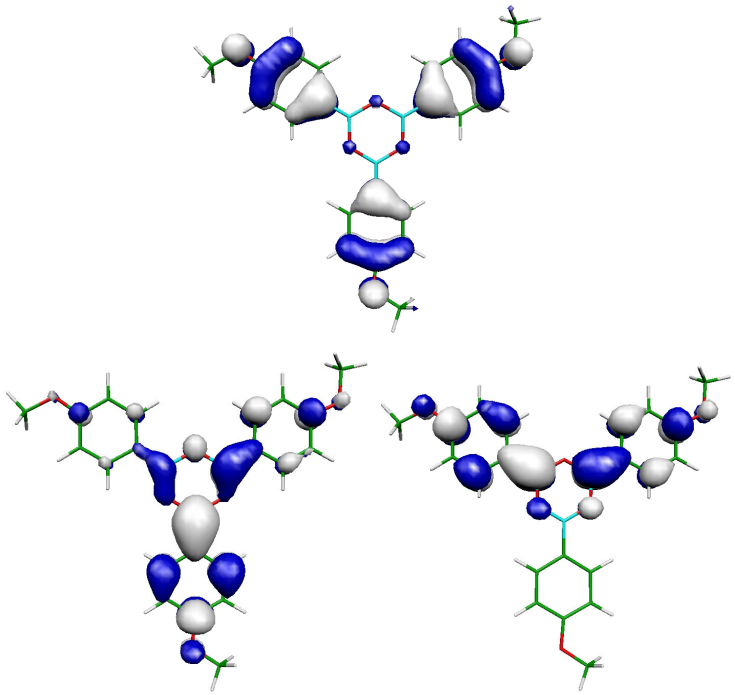

Fig. 7. Contour surfaces of HOMO (top) and degenerated LUMO, LUMO + 1 (bottom) of molecule **B1**.

3.2.2. Quadratic nonlinearities

Comparison of Hammett constants and β estimates (Table 3) indicates that increasing the donating strength of the substituents results in a significant enhancement of β. In fact, molecule **3** bears the strongest electron-releasing groups of the series and displays the largest molecular optical nonlinearity, in correlation with a stronger solvatochromism. When compared to the values reported for TIATB[26], a soluble analogue of TATB, all three compounds of this series show a marked increase, compound **B3** showing a first-order hyperpolarisability more than ten times larger while maintaining improved transparency. Even more, these compounds show better transparency-nonlinearity trade-off that tris-substituted triazines.[20,26,27,36] This shows that the "boroxine" molecular engineering route implemented here is well founded.

Calculated values reproduce global trends, however quantitative agreement with experimental values is poor. This is not surprising at least for three reasons. First, it is well known that conventional exchange-correlation functionals incorrectly describe the polarization of conjugated systems when it is due to donor/acceptor groups. It has also been shown that solvent effects, which are neglected in the present work, lead to significant enhancement of both linear and non linear polarizabilities.[69-70] In the case of TATB, enhancement of β can be up to a factor of 2 in highly polar solvents, and the solvent effects could be even somewhat larger for the boroxine derivatives investigated in this study. In addition, it is clear that (hyper)polarizabilities as well as dipole moments, are very sensitive to the size of the basis set, especially for diffuse functions. This calls for more sophisticated theoretical studies taking into account the above-mentioned considerations.

4. CONCLUSION

The present study demonstrates that the novel "boroxine" route towards improved octupoles for NLO indeed leads to molecules displaying markedly improved nonlinearity-transparency trade-off as compared to the prototypical organic octupole 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) or the widely studied octupolar triazine derivatives. Combined experimental and theoretical investigations reveal that this behavior is related to a periphery-to-core intramolecular charge transfer phenomenon in relation with the low-aromaticity and electron-withdrawing character of the boroxine ring. This study opens a new route for molecular engineering of transparent octupolar derivatives for NLO, for different applications including the design of effective materials for SHG in the visible-blue region. Further improvement of the nonlinear responses should be achieved before applications in EOM are considered. This could be done for instance by using similar strategies as those developed for triphenylbenzenes.[22-25] In addition, it would be particularly desirable to implement the smart crystal engineering routes that have proven successful for other 2-D octupolar derivatives.[35]

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REFERENCES

1. D. S. Chemla and J. Zyss, (Eds.): Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York, 1987.
2. J. Zyss and I. Ledoux, "Nonlinear Optics in Multipolar Media: Theory and Experiments", *Chem. Rev.* **94**, 77-105, 1994.
3. E. Goovaerts, W. E. Wenseleers, M. H. Garcia and G. H. Cross, in H.S. Nalwa (Ed.), Handbook of Advanced Electronic and Photonic Materials and Devices. Academic Press, 2001, p. 127-191.
4. Y. Shi, C. Zhang, H. Zhang, J. H. Bechtel, L. R. Dalton, B. H. Robinson and W. H. Steier, "Low (sub-1-volt) halwave voltage polymeric electro-optic modulators achieved by controlling chromophore shape", *Science* **288**, 119-122, 2000.
5. D. A. Parthenopoulos and P. M. Rentzepis, "Three-dimensional optical storage memory", *Science* **245**, 843-845, 1989.
6. S. Maruo, O. Nakamura and S. Kawata, "Three-Dimensional microfabrication with two-photon absorbed photopolymerization", *Opt. Lett.* **22**, 132-134, 1997.
7. B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X. L. Wu, S. R. Marder and J. W.

Perry, "Two-photon polymerization initiators for three-dimensional optical data storage and microfabrication", *Nature* **398**, 51-54, 1999.
8. S. Kawata, H.-B. Sun, T. Tanaka and K. Takada, "Finer features for functional microdevices", *Nature* **412**, 697-698, 2001.
9. W. Denk, J. H. Strickler and W. W. Webb, "Two-photon laser scanning fluorescence microscopy", *Science* **248**, 73-76, 1990.
10. L. Moreaux, O. Sandre, S. Charpak, M. Blanchard-Desce and J. Mertz, "Coherent scattering in multi-harmonic light microscopy", *Biophys. J.* **80**, 1568-1574, 2001.
11. M. Blanchard-Desce, V. Alain, P. V. Bedworth, S. R. Marder, A. Fort, C. Runser, M. Barzoukas, S. Lebus and R. Wortmann, "Large quadratic hyperpolarizabilities with donor-acceptor polyenes exhibiting optimum bond length alternation: correlation between structure and hyperpolarizability", *Chem. Eur. J.* **3**, 1091-1104, 1997.
12. V. Alain, M. Blanchard-Desce, I. Ledoux-Rak and J. Zyss, "Amphiphilic polyenic push-pull chromophores for nonlinear optical applications", *Chem. Commun.*, 353-354, 2000.
13. I. Ledoux, J. Zyss, J. S. Siegel, J. Brienne and J.-M. Lehn, "Second-harmonic generation from non-dipolar non-centrosymmetric aromatic charge-transfer molecules", *Chem. Phys. Lett.* **172**, 440-444, 1990.
14. J. Zyss, "Molecular engineering implications of rotational invariance in quadratic nonlinear optics: From dipolar to octupolar molecules and materials", *J. Chem. Phys.* **98**, 6583-6599, 1993.
15. J. J. Wolff and R. Wortmann, "Organic materials for nonlinear optics. The 2D approach", *J. Prakt. Chem.* **340**, 99-111, 1998.
16. J. J. Wolff and R. Wortmann, "Organic materials for second-order non-linear optics", *Adv. Phys. Org. Chem.* **32**, 121-217, 1999.
17. M. Joffre, D. Yaron, R. J. Silbey and J. Zyss, "Second order optical nonlinearity in octupolar aromatic systems", *J. Chem. Phys.* **97**, 5607-5615, 1992.
18. J.-L. Brédas, F. Meyers, B. M. Pierce and J. Zyss, "On the Second-Order Polarizability of Conjugated p-Electron Molecules with Octupolar Symmetry: the Case of Triaminotrinitrobenzene", *J. Am. Chem. Soc.* **114**, 4928-4929, 1992.
19. T. Verbiest, K. Clays, C. Samyn, J. Wolff, D. Reinhoudt and A. Persoons, "Investigations of the Hyperpolarizability in Organic Molecules from Dipolar to Octopolar Systems", *J. Am. Chem. Soc.* **116**, 9320-9323, 1994.
20. P. C. Ray and P. K. Das, "First-order hyperpolarizabilities of octupolar aromatic molecules: symmetrically substituted triazines", *Chem. Phys. Lett.* **244**, 153-156, 1995.
21. O. F. J. Noordman and N. F. van Hulst, "Time-resolved hyper-Rayleigh scattering: measuring first hyperpolarizabilities β of fluorescent molecules", *Chem. Phys. Lett.* **253**, 145-150, 1996.
22. J. Brunel, I. Ledoux, J. Zyss and M. Blanchard-Desce, "Propeller-shaped molecules with giant off-resonance optical nonlinearities", *Chem. Commun.*, 923-924, 2001.
23. J. Brunel, A. Jutand, I. Ledoux, J. Zyss and M. Blanchard-Desce, "Boomerang-shaped octupolar molecules derived from triphenylbenzene", *Synth. Met.* **124**, 195-199, 2001.
24. J. Brunel, A. Jutand, I. Ledoux, J. Zyss and M. Blanchard-Desce, "Nanoscale Boomerang-Shaped Octupolar Molecules Derived from Triphenylbenzene", *Proc. SPIE-Int. Soc. Opt. Eng.* **4798**, 29-36, 2002.
25. J. Brunel, O. Mongin, A. Jutand, I. Ledoux, J. Zyss and M. Blanchard-Desce, "Propeller-Shaped Octupolar Molecules Derived from Triphenylbenzene for Nonlinear Optics: Synthesis and Optical Studies", *Chem. Mater.* **15**, 4139-4148, 2003.
26. R. Wortmann, C. Glania, P. Krämer, R. Matschiner, J. J. Wolff, S. Kraft, B. Treptow, E. Barbu, D. Längle and G. Görlitz, "Nondipolar Structures with Threefold Symmetry for Nonlinear Optics", *Chem. Eur. J.* **3**, 1765-1773, 1997.
27. J. J. Wolff, F. Siegler, R. Matschiner and R. Wortmann, "Optimized Two-Dimensional NLO Chromophores with Threefold Symmetry Axis", *Angew. Chem., Int. Ed.* **39**, 1436-1439, 2000.
28. B. R. Cho, S. B. Park, S. J. Lee, K. H. Son, S. H. Lee, M.-J. Lee, J. Yoo, Y. K. Lee, G. J. Lee, T. I. Kang, M. Cho and S.-J. Jeon, "1,3,5-Tricyano-2,4,6-tris(vinyl)benzene Derivatives with Large Second-Order Nonlinear Optical Properties", *J. Am. Chem. Soc.* **123**, 6421-6422, 2001.
29. B. R. Cho, M. J. Piao, K. H. Son, S. H. Lee, S. J. Yoon, S.-J. Jeon and M. Cho, "Nonlinear optical and two-photon absorption properties of 1,3,5-tricyano-2,4,6-tris(styryl)benzene-containing octupolar oligomers", *Chem. Eur. J.* **8**, 3907-3916, 2002.

30. B. R. Cho, Y. H. Kim, K. W. Son, C. Khalil, Y. H. Kim and S.-J. Jeon, "Synthesis and nonlinear optical properties of 1,3,5-tricyano-2,4,6-tris[2-(thiophen-2-yl)vinyl]benzene derivatives", *Bull. Korean Chem. Soc.* **23**, 1253-1256, 2002.
31. B. R. Cho, S. J. Lee, S. H. Lee, K. H. Son, Y. H. Kim, J.-Y. Doo, G. J. Lee, T. I. Kang, Y. K. Lee, M. Cho and S.-J. Jeon, "Octupolar Crystals for Nonlinear Optics: 1,3,5-Trinitro-2,4,6-tris(styryl)benzene Derivatives", *Chem. Mater.* **13**, 1438-1440, 2001.
32. B. R. Cho, K. Chajara, H. J. Oh, K. H. Son and S.-J. Jeon, "Synthesis and Nonlinear Optical Properties of 1,3,5-Methoxy-2,4,6-tris(styryl)benzene Derivatives", *Org. Lett.* **4**, 1703-1706, 2002.
33. J. Zyss, S. Brasselet, V. R. Thalladi and G. R. Desiraju, "Octupolar versus dipolar crystalline structures for nonlinear optics: A dual crystal and propagative engineering approach", *J. Chem. Phys.* **109**, 658-669, 1998.
34. V. Thalladi, R., S. Brasselet, H.-C. Weiss, D. Bläser, A. K. Katz, H. L. Carrel, R. Boese, J. Zyss, A. Nangia and G. R. Desiraju, "Crystal Engineering of Some 2,4,6-Triaryloxy-1,3,5-triazines: Octupolar Nonlinear Materials", *J. Am. Chem. Soc.* **120**, 2563-2577, 1998.
35. V. Thalladi, R., R. Boese, S. Brasselet, I. Ledoux, J. Zyss, R. K. R. Jetti and G. R. Desiraju, "Steering non-centrosymmetry into the third dimension: crystal engineering of an octupolar nonlinear optical crystal", *Chem. Commun.*, 1639-1640, 1999.
36. S. Brasselet, F. Cherioux, P. Audebert and J. Zyss, "New Octupolar Star-Shaped Structures for Quadratic Nonlinear Optics", *Chem. Mater.* **11**, 1915-1920, 1999.
37. S. Stadler, F. Feiner, C. Bräuchle, S. Brandl and R. Gompper, "Determination of the first hyperpolarizability of four octupolar molecules and their dipolar subunits via hyper-Rayleigh scattering in solution", *Chem. Phys. Lett.* **245**, 292-296, 1995.
38. S. Stadler, C. Bräuchle, S. Brandl and R. Gompper, "Experimental Determination of the First Hyperpolarizability of New Chiral and Achiral Octupolar Tertiary Amines by Hyper-Rayleigh Scattering", *Chem. Mater.* **8**, 414-417, 1996.
39. C. Lambert, W. Gaschler, E. Schmälzlin, K. Meerholz and C. Bräuchle, "Subchromophore interactions in tricyanovinyl-substituted triarylamines-a combined experimental and computational study", *J. Chem. Soc., Perkin Trans. 2*, 577-587, 1999.
40. C. Lambert, W. Gaschler, G. Noll, M. Weber, E. Schmalzlin, C. Brauchle and K. Meerholz, "Cationic .pi.-electron systems with high quadratic hyperpolarizability", *J. Chem. Soc., Perkin Trans. 2*, 964-974, 2001.
41. B. R. Cho, S. K. Lee, K. A. Kim, K. N. Son, T. I. Kang and S. J. Jeon, "First hyperpolarizabilities of hexaazatriphenylene derivatives: octupolar nonlinear optical molecules", *Tetrahedron Lett.* **39**, 9205-9208, 1998.
42. P. J. A. Kenis, O. F. J. Noordman, S. Houbrechts, G. J. Van Hummel, S. Harkema, F. C. J. M. Van Veggel, K. Clays, J. F. J. Engbersen, A. Persoons, N. F. Van Hulst and D. N. Reinhoudt, "Second-Order Nonlinear Optical Properties of the Four Tetranitrotetrapropoxycalix[4]arene Conformers", *J. Am. Chem. Soc.* **120**, 7875-7883, 1998.
43. T. Verbiest, K. Clays, A. Persoons, F. Meyers and J.-L. Brédas, "Determination of the hyperpolarizability of an octopolar molecular ion by hyper-Rayleigh scattering", *Opt. Lett.* **18**, 525-527, 1993.
44. J. Zyss, T. Chau Van, C. Dhenaut and I. Ledoux, "Harmonic Rayleigh scatterinf from nonlinear octupolar molecular media: the case of crystal violet", *Chem. Phys.* **177**, 281-296, 1993.
45. T. W. Chui and K. Y. Wong, "Study of Hyper-Rayleigh scattering and two-photon absorption induced fluorescence from crystal violet", *J. Chem. Phys.* **109**, 1391-1396, 1998.
46. D. R. Greve, S. B. Schougaard, T. Geisler, J. C. Petersen and T. Bjørnholm, "Large Third-Order Nonlinear Optical Response from Molecules with Effective Multidirectional Charge-Transfer Transitions: new design of Third-Order Nonlinear Chromophores", *Adv. Mater.* **9**, 1113-1116, 1997.
47. S. Stadler, C. Bräuchle, S. Brandl and R. Gompper, "Determination of the First Hyperpolarizabilities of Octupolar Molecular Ions Made from Symmetric Cyanine Dyes", *Chem. Mater.* **8**, 676-678, 1996.
48. M. Lequan, C. Branger, J. Simon, T. Thami, E. Chauchard and A. Persoons, "First Hyperpolarizability of Organotin Compounds with Td Symmetry", *Adv. Mater.* **6**, 851-853, 1994.
49. C. Lambert, E. Schmälzlin, K. Meerholz and C. Bräuchle, "Synthesis and nonlinear optical properties of three-dimensional phosphonium ion chromophores", *Chem. Eur. J.* **4**, 512-521, 1998.
50. M. Blanchard-Desce, J.-B. Baudin, O. Ruel, L. Jullien, S. Brasselet and J. Zyss, "New non-dipolar structures with significant quadratic hyperpolarizabilities", *Opt. Mater.* **9**, 276-279, 1998.

51. M. Blanchard-Desce, J.-B. Baudin, L. Jullien, R. Lorne, O. Ruel, S. Brasselet and J. Zyss, "Towards highly efficient nonlinear optical chromophores: Molecular engineering of octupolar molecules", *Opt. Mater.* **12**, 333-338, 1999.
52. C. Bourgogne, Y. Le Fur, P. Juen, P. Masson, J.-F. Nicoud and R. Masse, "Tetra(4-methoxyphenyl)phosphonium Iodide: A Twinned Crystal Built Up with Three-Dimensional Octupolar Nonlinear Optical Chromophores", *Chem. Mater.* **12**, 1025-1033, 2000.
53. G. P. Bartholomew, I. Ledoux, S. Mukamel, G. C. Bazan and J. Zyss, "Three-Dimensional Nonlinear Optical Chromophores Based on Through-Space Delocalization", *J. Am. Chem. Soc.* **124**, 13480-13485, 2002.
54. G. Alcaraz, L. Euzenat, O. Mongin, C. Katan, I. Ledoux, J. Zyss and M. Blanchard-Desce, "Improved transparency-nonlinearity trade-off with boroxine-based octupolar molecules." *Chem. Commun.*, 2766-2767, 2003.
55. R. S. Klein, G. E. Kugel, A. Maillard, A. Sifi and K. Polgár, "Absolute non-linear optical coefficients measurements of BBO single crystal and determination of angular acceptance by second harmonic generation", *Opt. Materials*, **22**, 163-169, 2003.
56. 56. W.-H. Lee, H. Lee, J.-A. Kim, J.-H. Choi, M. Cho, S.-J. Jeon and B. R. Cho, "Two-Photon Absorption and Nonlinear Optical Properties of Octupolar Molecules", *J. Am. Chem. Soc.* **123**, 10658-10667, 2001.
57. (a) C. P. Brock, R. P. Minton and K. Niedenzu, "Structure and thermal motion of triphenylboroxin", *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C43**, 1775-1779, 1987; (b) M. A. Beckett, G. C. Strickland, K. Sukumar Varma, D. E. Hibbs, M. B. Hurthouse and K. M. Abdul Malik, *J. Org. Chem.,* **535**, 33-41, 1997.
58. (a) P. v. R. Schleyer, H. Jiao, N. J. R. v. E. Hommes, V. G. Malkin and O. L. Malkina, "An Evaluation of the Aromaticity of Inorganic Rings: Refined Evidence from Magnetic Properties", *J. Am. Chem. Soc.* **119**, 12669-12670, 1997; (b) P. W. Fowler and E. Steiner, "Ring Currents and Aromaticity of Monocyclic -Electron Systems C6H6, B3N3H6, B3O3H3, C3N3H3, C5H5-, C7H7+, C3N3F3, C6H3F3, and C6F6", *J. Phys. Chem. A*; **101**, 1409-1413, 1997.
59. Y. Tokunaga, H. Ueno, Y. Shimomura and T. Seo, "Formation of boroxine: its stability and thermodynamic parameters in solution", *Heterocycles* **57**, 787-790, 2002.
60. R. W. Terhune, P. D. Maker and C. M. Savage, "Measurements of nonlinear light scattering", *Phys. Rev. Lett.* **14**, 681-684, 1965.
61. P. D. Maker, "Spectral Broadening of Elastic Second-Harmonic Light Scattering in Liquids", *Phys. Rev. A* **1**, 923-951, 1970.
62. K. Clays and A. Persoons, "Hyper-Rayleigh Scattering in Solution", *Phys. Rev. Lett.* **66**, 2980-2983, 1991.
63. I. Ledoux, C. Dhenaut, I. D. W. Samuel and J. Zyss, "Octupolar metal complexes for quadratic nonlinear optics", *Nonlinear Opt.* **14**, 23-37, 1995.
64. A. Willets, J. E. Rice, D. M. Burland and D. P. Shelton, "Problems in the comparison of theoretical and experimental hyperpolarizabilities", *J. Chem. Phys.* **97**, 7590-7599, 1992.
65. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, R. E. S. and J. A. Pople: Gaussian 98, Revision A.11, Gaussian, Inc., Pittsburgh PA, 2001.
66. A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange", *J. Chem. Phys.* **98**, 5648-5652, 1993.
67. MOLEKEL 4.0; P. Flükiger, H. P. Lüthi, H., S. Portmann and J. Weber, Swiss Center for Scientific Computing, Manno (Switzerland), 2000.
68. C. Hansch, A. Leo and R. W. Taft, "A Survey of Hammett Substituent Constants and Resonance and Field Parameters", *Chem. Rev.* **91**, 165-195, 1991.
69. Y. Luo, P. Norman and H. Ågren, "Onsager Reaction Field Description of Optical Properties of Octupolar Molecules in Solution", *J. Am. Chem. Soc.* **120**, 11188-11189, 1998.
70. C. Dehu, V. Geskin, A. Persoons and J.-L. Brédas, "Effect of Medium Polarity on the Second-Order Polarizability of an Octupolar Chromophore: An ab initio Reaction Field Study of Triaminotrinitrobenzene", *Eur. J. Org. Chem.,* 1267-1269, 1998.